Bureau of Mines Report of Investigations/1987

Leaching of Phosphate Values From Two Central Florida Ores Using H_2SO_4-Methanol Mixtures

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UNITED STATES DEPARTMENT OF THE INTERIOR

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	in	inch
cm	centimeter	lb	pound
ft	foot	lb/(h·ft^2)	pound per hour per square foot
ft^3/min	cubic foot per minute	min	minute
g	gram	mL	milliliter
gal	gallon	pct	percent
gal/min	gallon per minute	s	second
h	hour		

LEACHING OF PHOSPHATE VALUES FROM TWO CENTRAL FLORIDA ORES USING H_2SO_4-METHANOL MIXTURES

By G. M. Wilemon[1] and B. J. Scheiner[2]

ABSTRACT

The Bureau of Mines conducted preliminary investigations on the use of an acid-alcohol leaching technique for recovering phosphate values from phosphate matrices. H_2SO_4 and methanol were used as the leaching agents. Starting-matrix particle size and acid-apatite ratio were found to significantly affect the efficiency of phosphate leaching. Phosphate extractions of more than 80 pct were obtained when minus 200-mesh ore was used and the acid-apatite ratio was 8:1 or more. The iron and aluminum oxide impurities (R_2O_3) present in the crude acid products were monitored, and R_2O_3-P_2O_5 ratios are reported. Phosphate extractions in excess of 80 pct also were obtained when phosphatic clay wastes were leached. Typically, leach slurries filtered using test leaf filters exhibited filtration rates of 100 lb/(h·ft^2) or more.

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INTRODUCTION

Wet-process phosphoric acid (H_3PO_4) is generated by treating phosphate rock with H_2SO_4 and is an important component in the manufacture of agricultural fertilizers (1).[3] In this country, the leading producer of phosphate rock is the State of Florida. The present practice is to mine the phosphate ore, also called matrix, using a dragline and then to slurry the ore with water in order to pump it to a beneficiation plant (2-4). Phosphate values are recovered from the plus 150-mesh fraction of the matrix slurry using a combination of screening and flotation steps. Conversely, phosphate values cannot be economically recovered from the minus 150-mesh fraction of the ore slurry. This fine-particle fraction, often called phosphatic clay waste or phosphate slime, currently is discarded by pumping it to impoundment areas called slime ponds. Approximately one-third of the total phosphate that was originally resident in the matrix is contained in the clay waste. The rate of flow of phosphatic clay waste to these settling areas ranges between 15,000 and 80,000 gal/min, and its solids content is only 2 to 6 pct. Because of the colloidal character of the waste, it settles very slowly, and after years it may still contain more than 70 pct water. To accommodate the waste, impoundment areas covering 400 to 600 acres with dam heights ranging from 20 to 60 ft are required. Currently, these clay waste slime ponds cover about 80,000 acres in Florida (5-6). Thus, not only is potentially valuable phosphate discarded with the minus 150-mesh fraction, but also the manner of the disposal, which ties up large quantities of land and water, is a major environmental concern.

One approach to increasing the recovery of phosphate and reducing the formation of slimes is to leach phosphate values directly from phosphate matrix, i.e., from ore that has not been beneficiated. Attempts to do this using H_2SO_4 as the leaching agent have resulted in phosphate recoveries as high as 90 pct (7-8). However, the crude acids obtained were not suitable as fertilizer precursors (8-9) because of iron and aluminum impurities. Also, filtration to separate the crude H_3PO_4 from the insoluble residue was slow and difficult (8) or required flocculant additives (7).

Other researchers have investigated the direct acidulation of phosphate ore using a mixture of H_2SO_4 and methanol as the leaching agent (10). The methanol both served as a solvent for the resultant H_3PO_4 and depressed the solubility of the iron and aluminum impurities. Thus, a crude acid suitable for the preparation of fertilizers was obtained by filtering the reaction mixture and distilling the methanol from the filtrate. Phosphate recoveries of 60 to 65 pct were reported (10).

Unfortunately, even though the acid-alcohol leaching of phosphate matrix appears to be potentially useful, few fundamental details of the technique have been reported. Information on this technique would be helpful in determining the advantages and disadvantages of total matrix acidulation as compared with other methods of phosphate processing. In this paper, a study of the acid-alcohol leaching of two phosphate ores from central Florida is presented. The effects of various parameters on the efficiency of phosphate leaching and on the amount of leached impurities are discussed. The effects of varying the H_2SO_4-apatite ratio, temperature, matrix particle size, and ore type are examined. Also, the effect of pretreating matrix with H_3PO_4 prior to leaching is discussed. Experiments also were conducted in which phosphatic clay wastes were used as feedstocks for acid-alcohol leaching. Finally, data on the rate of filtration of leach slurries are presented.

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[3]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

TABLE 1. - Chemical composition of phosphate matrices, percent

Analysis	Matrix	
	Hopewell	Agrico
P_2O_5.....................	15.4	22.7
Al_2O_3.....................	8.0	2.6
CaO.....................	2.5	1.1
F.....................	18.9	31.3
Fe_2O_3.....................	49.2	37.0
MgO.....................	1.2	2.0
SiO_2.....................	1.0	.4

TABLE 2. - Qualitative XRD analysis of phosphate ores

Mineral	Relative amount in matrix	
	Hopewell	Agrico
Quartz........	Major...........	Major.
Apatite.......	...do...........	Do.
Smectite......	Minor-major......	Minor.
Kaolinite.....	Trace...........	Trace.
Illite........	...do...........	Do.
Microcline....	...do...........	Do.
Wavellite.....	...do...........	ND.

ND Not determined.

PREPARATION AND DESCRIPTION OF PHOSPHATE MATRICES

Samples of phosphate matrix were obtained from Hopewell Land Corp. and from Agrico Mining Co.'s Fort Green Mine. Each ore sample was crushed to minus 1/4 in. The ores were air-dried for several days and then characterized by elemental and X-ray diffraction analysis (XRD). The results of these analyses are given in tables 1 and 2. The analyses indicated that the Agrico ore was a higher grade ore, containing about 50 pct more P_2O_5 than the Hopewell ore. Also, the Agrico matrix contained about one-third as much aluminum and less than half as much iron as its Hopewell counterpart.

EQUIPMENT AND PROCEDURES

Leaching experiments were conducted in a three-neck, 500-mL, round-bottom flask that was equipped with an overhead stirrer, a pressure-equilibrating dropping funnel, and a reflux condenser. In each experiment, the flask was charged with 100 g matrix and 200 mL methanol. The resulting mixture was stirred vigorously and heated to reflux temperature (approximately 65° C). The desired quantity of technical-grade sulfuric acid (93 pct H_2SO_4) was then placed in the dropping funnel and added dropwise to the refluxing slurry over a period of 30 min. After the acid addition was complete, stirring and heating were continued for an additional 30 min. Then the mixture was cooled to room temperature and vacuum-filtered through Whatman[4] No. 3 filter paper to separate the phosphate-containing liquid from the insoluble residue. The residue was washed twice with 200-mL aliquots of methanol and then dried in an oven at 110° C. The filtrate and washings were combined, and the methanol was removed and recovered for recycle using a rotary evaporator. Elemental analyses were obtained on both the crude phosphoric acid product and the leach residue. Additionally, leach residues were analyzed using XRD.

The mineral apatite, which usually exists in the form of fluorapatite ($Ca_5(PO_4)_3F$), is leached from phosphate matrix by the H_2SO_4. However, phosphate matrix contains other minerals that also can react with H_2SO_4 (e.g., reactive silicates or CaO). Thus, more acid is needed than that required for the apatite content alone. Furthermore, acid requirements could vary as reaction conditions vary. Because of these factors, it was difficult to determine in advance the optimum amount of acid to use. Therefore, in these experiments, each variable that was evaluated was done so over a range of amounts of acid added. This was all put on a relative basis by

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[4]Reference to specific products does not imply endorsement by the Bureau of Mines.

Page 3, Table 1:

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CaO....................	18.9	31.3
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Fe_2O_3....................	2.5	1.1
MgO....................	1.0	.4
SiO_2....................	49.2	37.0

using a calculated acid-to-apatite (Ap) molar ratio.

It is generally accepted that the reaction between fluorapatite and H_2SO_4 to yield H_3PO_4 takes place according to the following stoichiometry (7):

$$Ca_5(PO_4)_3F + 5H_2SO_4 + 10H_2O$$

$$\rightarrow \quad H_3PO_4 + 5(CaSO_4 \cdot 2H_2O) + HF.$$
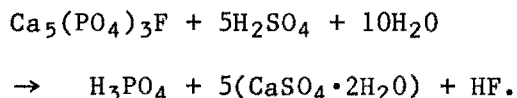
Since XRD analysis did not indicate the significant presence of any other phosphorus-containing materials, it was assumed that all of the phosphorus in the Hopewell and Agrico ores was in the form of apatite. Of course, apatite does not exist as discrete molecules but rather as a crystalline lattice. Nonetheless, the use of the same equation does allow meaningful comparisons to be made between leaching experiments when varying amounts of H_2SO_4 are used. Thus, 5 moles of acid for each "mole" of apatite was considered stoichiometric. Acid-Ap ratios in these experiments ranged from 4:1 to 16:1.

When phosphate matrix is treated with H_2SO_4, competing reations occur that leach undesirable impurities from the ore as well as the phosphate values (3, 7). Two of the most significant contaminants in wet-process acid are Al_2O_3 and Fe_2O_3. When aluminum or iron is present in a crude acid product in sufficiently large quantities, it renders the crude acid less suitable as a fertilizer precursor. Because the effects of these two contaminants are similar, they are frequently taken together as the R_2O_3 content of a given acid product. The $R_2O_3-P_2O_5$ ratio of an acid product is often used to determine whether an acid can reasonably be used to prepare fertilizer. If the $R_2O_3-P_2O_5$ ratio is 0.1 or greater, the acid is considered unsuitable (3). Therefore, in these leaching experiments, the Al_2O_3 and Fe_2O_3 contents of both the matrix and the resulting acids were determined via elemental analysis, and the $R_2O_3-P_2O_5$ ratios in the crude acid products are reported.

EFFECT OF TEMPERATURE

The effect of reaction temperature on the efficiency of phosphate leaching was evaluated by conducting experiments at three temperatures: ambient, 40°, and 65° C (the reflux temperature of methanol). The experiments were conducted at three different acid-Ap ratios using Hopewell matrix that previously had been ground to minus 100 mesh. Because the leaching reaction is exothermic, the experiments at ambient temperatures and at 40° C were conducted in a constant-temperature bath. Even so, the actual reaction temperature in these cases sometimes rose as much as 4° above the desired reaction temperature. The results of the experiments are shown in figure 1.

Phosphorus extraction was calculated by subtracting the amount of phosphorus in the leach residue from the amount present in the ore before leaching and dividing that difference by the amount of phosphorus present before leaching. The $R_2O_3-P_2O_5$ ratio was obtained by adding

the amount of Fe_2O_3 and Al_2O_3 found in the crude acid and dividing by the amount of P_2O_5 found in the crude acid. As figure 1 shows, both the $R_2O_3-P_2O_5$ ratio and the amount of phosphorus removed slightly increased as the temperature and/or the acid-Ap ratio increased. For example, when the acid-Ap ratio was 12:1, approximately 13 pct more phosphorus was extracted from the ore at 65° C than at 40° C. However, the $R_2O_3-P_2O_5$ ratio under these conditions rose from 0.15 to 0.23. The only experiment that yielded an acceptable $R_2O_3-P_2O_5$ ratio (0.08) was the one conducted at room temperature using a less than stoichiometric amount of acid. That experiment, however, leached only 59 pct of the phosphate values from the matrix, a recovery that can be achieved using current techniques. As refluxing conditions yielded slightly higher phosphorus extractions from the Hopewell ore, and as Wilson and Raden (10) previously
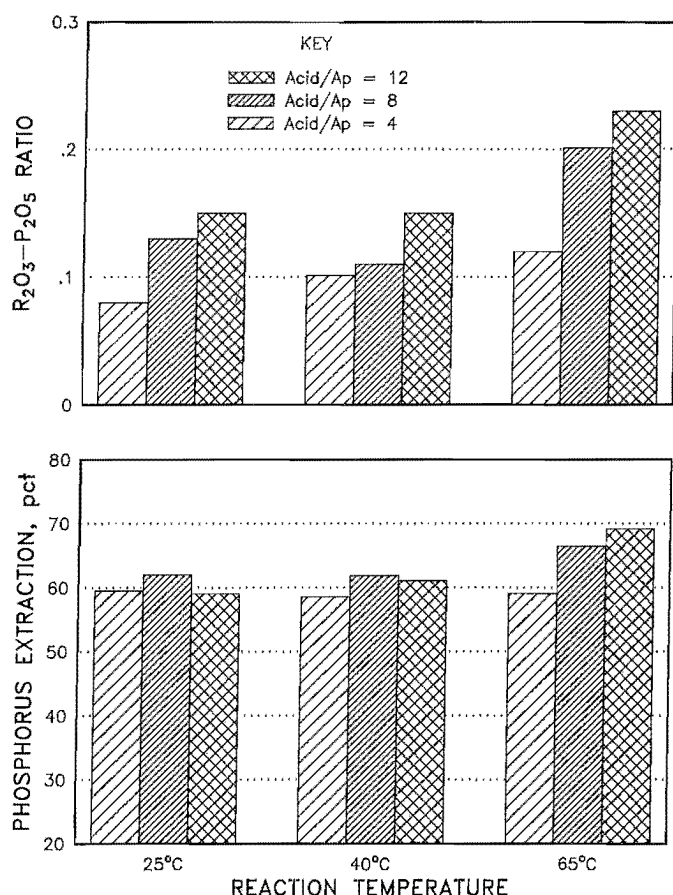
FIGURE 1.—Effect of reaction temperature on phosphate extraction and on R_2O_3-P_2O_5 ratio for Hopewell matrix.
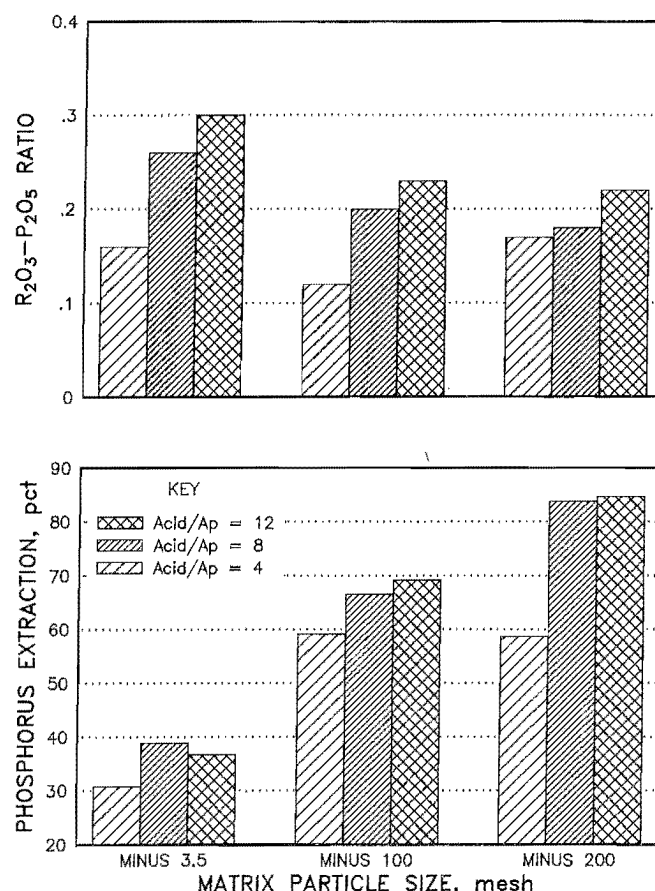
FIGURE 2.—Effect of starting-matrix particle size on phosphate extraction and on R_2O_3-P_2O_5 ratio for Hopewell matrix.

suggested that the preferred leaching temperature was the boiling point of the solvent, all subsequent experiments were conducted under reflux conditions.

EFFECT OF MATRIX PARTICLE SIZE

The effect of the particle size of the starting matrix was initially investigated using Hopewell ore that had been ground to three sizes: minus 3.5 mesh, minus 100 mesh, and minus 200 mesh. Also, each of these samples was evaluated at acid-Ap ratios of 4:1, 8:1, and 12:1. The results of these experiments are shown in figure 2 for the Hopewell ore and in figure 3 for the Agrico ore. The amount of phosphorus extracted from the ore rises sharply as the starting particle size is reduced, probably owing to the increase in surface area that accompanies size reduction. Phosphorus

extractions in excess of 80 pct were obtained when minus 200-mesh matrix was used and the acid-Ap ratio was 8:1 or greater. The minus 3.5-mesh ore, however, did not give very good recoveries. This was an unexpected and disappointing result, because previous reports had suggested that the acid-alcohol technique would work well on particles ranging in size from 1/2 to 1/4 in (10).

All of the experiments with Hopewell matrix generated crude acid products that contained excessive amounts of iron and aluminum impurities. The R_2O_3-P_2O_5
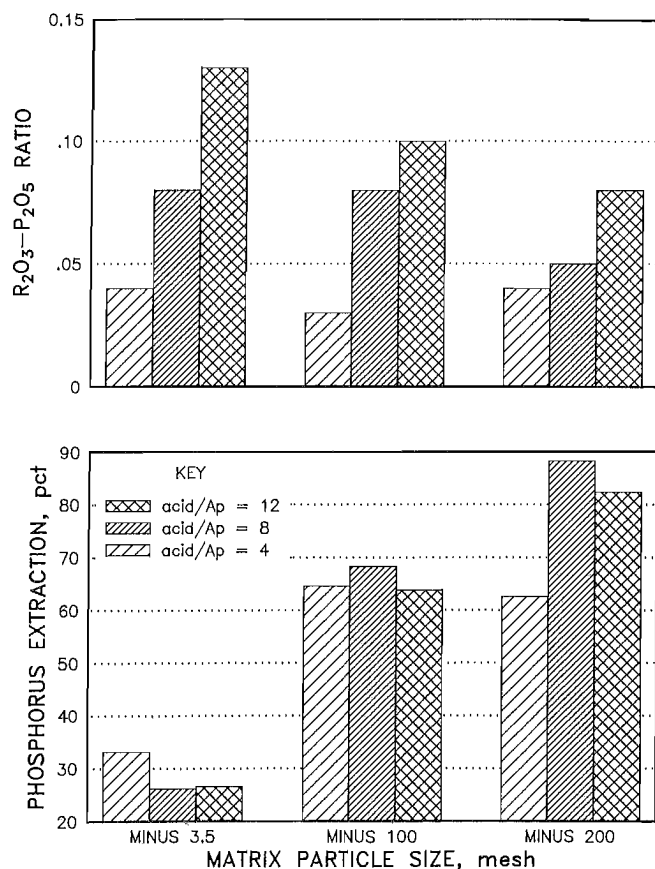
FIGURE 3.—Effect of starting-matrix particle size on phosphate extraction and on R_2O_3-P_2O_5 ratio for Agrico matrix.

FIGURE 4.—Effect of pretreatment with phosphoric acid on phosphate extraction and on R_2O_3-P_2O_5 ratio for phosphate matrices.

ratios, however, did decrease significantly as the particle size was reduced from minus 3.5 mesh to minus 100 mesh. Unfortunately, no further decreas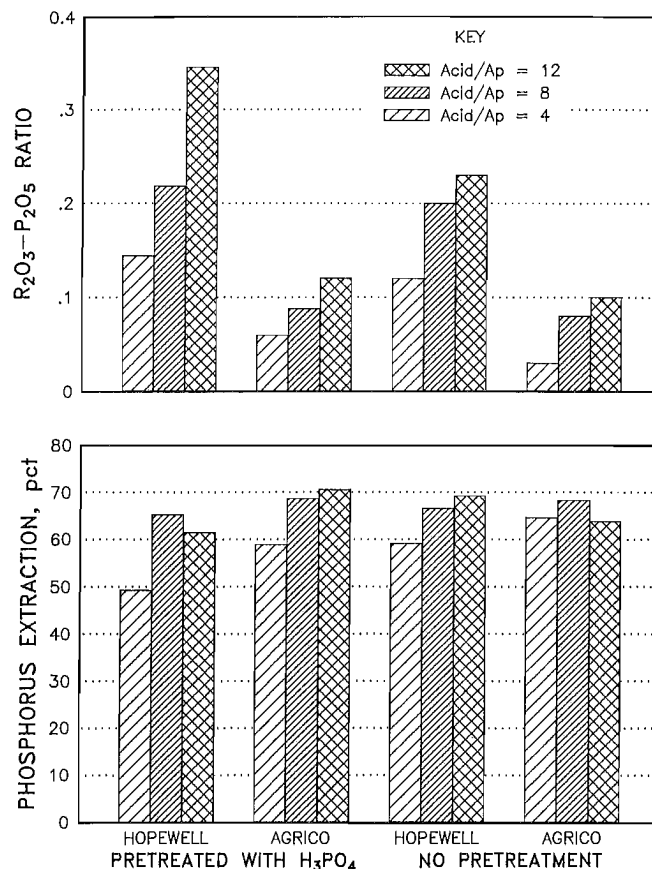e occurred when the particle size was reduced to minus 200 mesh. Agrico matrix gave a satisfactory R_2O_3-P_2O_5 ratio for either minus 100-mesh or minus 200-mesh particle size.

EFFECT OF PRETREATMENT WITH PHOSPHORIC ACID

The experiments with varying matrix particle size showed that phosphorus extraction of 80 pct or more are possible for both ores, when the matrix is minus 200 mesh and the acid-Ap ratio is 8:1 or greater. However, the minus 100-mesh matrices, when leached under the same conditions, gave extractions of only approximately 65 pct. XRD and energy-dispersive spectroscopy (EDS) analysis of the residues from the leaching experiments indicated that the residual phosphorus in the leach residues from these experiments is still in the form of apatite. One possible cause of the

unreactivity of the apatite mineral is that, when phosphate rock is treated with H_2SO_4, it can react to form gypsum so quickly that unreacted apatite particles are coated and rendered inert to further acidulation. In standard wet processing of phosphate rock concentrates, pretreatment with recycled H_3PO_4 is used to minimize gypsum coating. To determine if pretreatment with H_3PO_4 prior to treatment with H_2SO_4 would help in these leaching reactions, a series of experiments was conducted on the minus 100-mesh Hopewell and Agrico matrices. Enough 85-pct H_3PO_4 acid was added to each sample that the
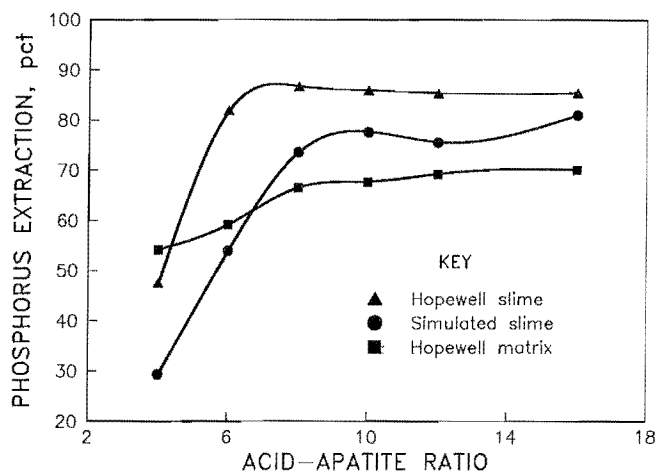
FIGURE 5.—Acid-alcohol leaching of Hopewell slime, simulated slime, and Hopewell matrix.

H_3PO_4 concentration, prior to sulfate addition, was 20 pct, the approximate strength of recycle acid in a wet-process plant. After the H_3PO_4 addition, the slurry was heated to reflux and stirred for 1 h. The desired amount of H_2SO_4 then was added as described earlier. The results of these experiments are shown in figure 4. Unfortunately, no significant difference was observed in the leaching of the pretreated samples compared with those that had not been pretreated. In fact, the pretreated samples gave slightly lower phosphorus extractions than those not pretreated.

LEACHING OF PHOSPHATE SLIMES

To determine whether phosphate slimes could be leached using the acid-alcohol technique, a sample of slime was obtained from Hopewell Land Corp. The slime was received as a slurry containing 1.36 pct solids. In addition, a "simulated" slime was prepared by wet-screening a portion of the Hopewell matrix through a 150-mesh screen. The Hopewell slime and the simulated slime were allowed to settle for several days, and then clear water was decanted from each of them. The thickened slurries then were dried, and the residues were crushed to pass a 100-mesh screen. Elemental analyses of these residues are presented in table 3. To compare the leaching of the Hopewell and simulated slimes with that of the Hopewell matrix, all three materials were used as feedstocks for several leaching experiments. The three materials were leached at six different acid-Ap ratios: 4:1, 6:1, 8:1, 10:1, 12:1, and 16:1. The resultant filter cake from each experiment was washed, dried, and submitted for elemental analysis. The results of these experiments are shown in figure 5.

Good phosphorus extractions were observed in the leaching of both the simulated slime and the Hopewell slime. More than 70 pct of the phosphorus in the simulated slime was removed when the acid-Ap ratio was 8:1 or greater. The Hopewell slime gave even better results; extractions of 80 pct were observed when the acid-Ap ratio was 6:1 or more. These results are encouraging in that they suggest that phosphate slimes could be a legitimate source of phosphate if an economical method could be found to dewater them.

TABLE 3. – Chemical composition of phosphate slimes, percent

Analysis	Slime	
	Hopewell	Simulated
P_2O_5...................	12.5	7.3
Al_2O_3................	13.9	14.4
Fe_2O_3................	2.9	2.6
CaO...................	20.3	11.5
SiO_2.................	43.7	55.7
F....................	1.0	.7
MgO...................	1.2	1.3

FILTRATION OF LEACH SLURRIES

Filtration tests were conducted to determine the rate of filtration of leach residue through a variety of filter cloths stretched over a leaf filter having a diameter of 10.3 cm. The slurries used in the tests were prepared by leaching minus 100-mesh and minus 200-mesh Hopewell matrices using an 8:1 acid-

TABLE 4. - Filtration of leach slurries from Hopewell ores

Filter cloth	Porosity,[1] ft³/min	Material	Filament	Weave	Filtration rate, lb/(h·ft²)	
					Minus 100 mesh	Minus 200 mesh
SPN 302...	1	Nylon........	Multifilament	Sateen.....	86	122
SPD 152...	1- 2	Dacron.......	...do........	2 × 2 twill	61	146
SPD 276Q..	1- 2	...do........	Continuous...	...do......	44	160
SPP 39M...	2	Polypropylene	Multifilament	Oxford.....	65	151
SPD 398...	2.3	Dacron.......	...do........	Plain......	49	[2]170
SPP 105...	2- 3	Polypropylene	Continuous...	Chain......	99	177
SPP 10....	3- 5	...do........	Multifilament	Plain......	46	173
SPD 582...	15- 20	Dacron.......	...do........	2 × 2 twill	54	165
SPP 540...	20- 30	Polypropylene	...do........	...do......	99	138
SPA 203...	27- 28	Acrilan......	...do........	3 × 2 twill	96	145
RN 5066...	30	Nylon........	...do........	2 × 2 twill	89	[2]146
SPD 285...	40- 50	Dacron.......	...do........	...do......	88	146
SPP 924...	120	Polyethylene.	Monofilament	Plain......	98	146
RN 2309 F.	200	Nylon........	...do........	...do......	122	NAp

NAp Not applicable.
[1]Porosity numbers were supplied by manufacturer.
[2]A substantial amount of slime passed through in these tests.

Ap ratio. The filtration test procedure involved placing the cloth-covered test leaf in a rapidly stirred leach slurry for 30 s under a differential pressure of 20 Torr. The leaf was then removed from the slurry and placed in a upright position, and air was pulled through it for an additional 30 s. The filter cake then was removed from the cloth, dried, and weighed. Filtration rates were calculated as pounds of dry solids per hour per square foot of filter. The results of the filtration tests are given in table 4.

As shown in table 4, many of the test slurries gave filtration rates in excess of 100 lb/(h·ft²), especially those in which the minus 200-mesh material was used.

CONCLUSIONS

Studies on the leaching of phosphate values from two central Florida matrices have been conducted using a mixture of H_2SO_4 and methanol as leaching agent. Starting-matrix particle size and acid-Ap ratio significantly affected the efficiency of the phosphate leaching. Phosphate extractions of more than 80 pct were observed for both the Hopewell and Agrico ores when the starting-matrix particle size was minus 200 mesh and the acid-Ap ratio was 8:1 or more. Phosphate extractions of greater than 80 pct have also been obtained when phosphatic clay waste was used as feed material. These recoveries compare favorably with the approximately 60-pct recoveries that are obtained using the conventional beneficiation-acid treatment technique. However, at this time, only the Agrico ore has yielded crude acid products low enough in iron and aluminum to be considered viable fertilizer precursors.

The filtration of the leach slurries generated in these experiments was not difficult, and rates of over 100 lb/(h·ft²) were obtained for several of the filter cloths that were used.

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